ADVANCEMENT OF ELECTRICAL CHEMISTRY.

IN a previous article (March 1, p. 428) upon the advancement of electrical chemistry, various developments of electro-metallurgy or electrical deposition of metals were described. Electrolytic processes for obtaining the non-metallic elements and for the preparation of inorganic and organic compounds were left for consideration in a separate article, and are now dealt with.

In the year 1800, Nicholson and Carlisle showed that water could be decomposed into oxygen and hydrogen by means of a "volta pile"; since that time the electrolytic decomposition of water has been employed as a lecture experiment to show the composition of water. It is, however, only quite recently that oxygen and hydrogen have been produced on a manufacturing scale by the electrolysis of dilute solutions of caustic soda or sulphuric acid. The hydrogen so obtained is usually almost absolutely pure, but the oxygen is generally mixed with about 3 per cent. of hydrogen, which, however, can be removed by passing it through red-hot tubes.

The powerful oxidising action of ozone has through the advancement of electrical science been pressed into the service of the manufacturer. The methods employed for its production are all more or less based upon the well-known Siemen's tube. Generally speaking, air and not oxygen is ozonised, the air to be ozonised being freed from dust and from excess of moisture, the last of which causes formation of hydrogen peroxide. The temperature should be kept as low as possible, because at low temperatures oxides of nitrogen are less liable to be formed and the quantity of atmospheric oxygen converted into ozone is increased; indeed, some manufacturers cool the air down to 4° C. before subjecting it to the electric discharge. For convenience of use the ozone is generally compressed into iron cylinders under a pressure of from four to five atmospheres. It is used for refining and bleaching linseed and palm oils, and for the manufacture of oxidised oil for linoleum. Brewers are often troubled with fouling of the beer barrels; this seems to be due to the growth of a fungus which often penetrates the wood to a considerable depth, so that ordinary methods of cleansing fail to remove it. The oxidising action of ozone has been successfully employed to remove this growth, the method being to alternately steam and ozonise the casks. It has also been utilised to remove fusel oil from alcohol, in the purifying of water, the refining of sugar in place of animal charcoal, and in a great variety of other manufacturing processes.

It is well known that synthetical diamonds have been obtained by means of the electric furnace; charcoal obtained from sugar is rammed into a wrought iron cylinder, which is then closed with a plug. The cylinder so filled is placed in a bath of molten iron kept at a high temperature in an electric furnace, after which the crucible which contains the iron is rapidly cooled by immersion in melted lead. On dissolving the iron in acid minute diamonds are obtained. It was a question whether here we had a case of simple crystallisation of the carbon from the molten metal on cooling, or whether the enormous pressure which was exerted upon the interior of the mass by the rapid cooling of the outside acting upon the carbon at a high temperature caused the formation of crystals of diamond. An exceedingly ingenious experiment which has been carried out by Majorana shows that at any rate the influence of high pressure and high temperature combined is sufficient to convert amorphous carbon into the crystalline variety. Majorana's experiment is as follows:—

A cylindrical chamber, A (Fig. 1), is hermetically closed at the top by a solid block of iron, E, the bottom by a solid piston, S. The sides of the chamber are made of tempered steel, and to further strengthen it the chamber is surrounded by fifteen iron rings 1 cm. thick, which are bolted together. The whole system is placed within an hexagonal frame, K, also made from iron plates. The piston, S, has a small solid iron cylinder about 1 cm. in diameter attached to it, at the end of which is fastened a small piece of carbon, C, about 2 grms. in weight. Directly below the piston a thick block of iron, p, is fixed, into which a hole exactly the size of the small end of the cylinder has been drilled. In carrying out the experiment the carbon is heated by means of the two carbon poles, D, D', with a current of 25 amperes and 100 volts. When the carbon has become white-hot, 70 grms. of gunpowder contained in the chamber A is exploded, the piston being driven down, carrying the heated

carbon before it and compressing it with enormous force. On taking the system to pieces the carbon is found to have been partially converted into microscopic diamonds, which when freed from unchanged amorphous carbon are found to possess all the characteristics of natural diamonds.

Reference has already been made to the importance of the manufacture of calcium carbide; another carbide, that of silicon, is now being manufactured in considerable quantities, and, owing to its extreme hardness, is being employed in place of emery for polishing steel and making grindstones. This carbide, which goes under the name of "carborundum," is manufactured by means of the electric furnace. An American company at Niagara Falls employs furnaces capable of dealing with ten tons of material, consisting of coke, sand, common salt and sawdust, which yield two tons of carborundum in twenty-four hours. In the first half of the year 1897 it is stated that in America alone 750,000 lbs. of carborundum were manufactured. Since the introduction of electricity to chemistry the carbides of almost all the metals have been obtained, the majority naturally being more of theoretical than of commercial interest.

From the days of Leblanc, the founder of the soda industry, perhaps no branch of inorganic chemistry has been more worked at, or has better shown the results of patient toil and inventive genius, than the alkali and bleaching industry. Only after many attempts and many failures has the seemingly simple task of electrolysing sodium and potassium chloride yielded results
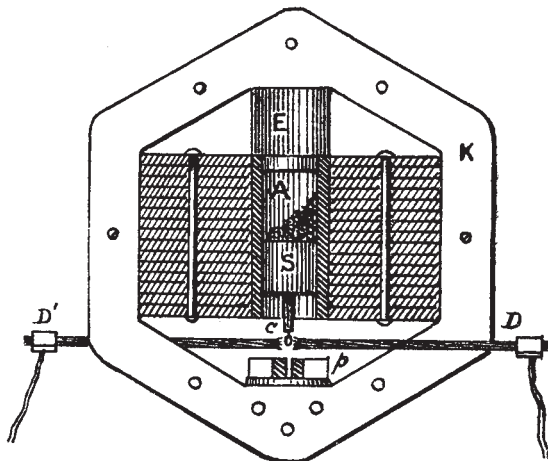

FIG. 1.

which have enabled electricity to enter into competition with the former methods of manufacture.

According to the manner in which the electrolysis is conducted, a solution of potassium chloride may be converted into chlorine and caustic potash, potassium hypochlorite, or into potassium chlorate. If the electrolysis takes place at low temperatures, a solution of hypochlorite is obtained, which may without further treatment be used for bleaching purposes. The difference in price between this solution and a solution of bleaching powder is not very great, but the greater cleanliness and purer bleaching action of potassium (sodium) hypochlorite make it, when electric power can be easily obtained, at least a powerful competitor with bleaching powder. When the electrolysis is conducted at temperatures from 60° and upwards, the bath being kept slightly alkaline by addition of potassium bicarbonate or lime, potassium chlorate is produced, which, owing to its slight solubility in water, crystallises out, and by washing is readily freed from adhering chloride.

If caustic potash and chlorine are required, some arrangement must be made to prevent the liberated chlorine from again reacting with the caustic potash formed at the same time. Formerly, and still to a small extent, this was arranged by means of a diaphragm which separated the anode from the kathode. Owing, however, to the difficulty of obtaining a *pervious impervious* diaphragm, *i.e.* one which allows the current to pass, but is impervious to the solution, it is now more general to electrolyse without a diaphragm. The method employed is one which was originally employed by Castner and

Kellner, the kathode being a layer of mercury at the bottom of the bath. On the current being passed, the potassium liberated at the kathode dissolves in it, forming an amalgam, which as it is formed is drawn off and run into pure water, the water being decomposed, assisted by an auxiliary current, with evolution of hydrogen and formation of caustic potash, which is obtained in the pure condition by evaporation. Carbonate of potash may be prepared by passing a stream of carbonic acid gas into the caustic liquors before evaporation. In commerce, naturally, it is more general to electrolyse the cheaper sodium chloride, at any rate, in this country. Strontium and barium chlorate are also manufactured by electrolysis of their chlorides.

It has been found possible to prepare painters' colours by electrolysis, *e.g.* " white lead " is obtained in a very pure condition by electrolysing a dilute solution of sodium chlorate and carbonate, the electrodes being of lead. If the sodium carbonate is replaced by sodium chromate, a neutral lead chromate is produced, an acid chromate being formed by cautious addition of a solution of chromic acid during the electrolysis.

To attempt to mention, much less to describe, the enormous number of inorganic compounds and elements which have been prepared or isolated by the aid of electricity, would be, in an article such as this, impossible ; but sufficient examples have been given to show the importance of electrical processes in this branch of chemistry.

Turning now to organic chemistry, we notice that, although a vast amount of work has been done, it is more of theoretical interest than of technical value. But now that the initial difficulties have been to a large extent overcome, and the manner in which the reactions take place is better understood, it is probable that shortly this branch of manufacturing chemistry will also undergo a revolution in the hand of the electro-chemist. As a means of synthesis and of proving the formula of substances, electrolysis has been, and is, of great value to the organic chemist. Thus on electrolysing a solution of an alkaline acetate, ethane is produced ; whereas by employment of a succinate, ethylene is formed, a solution of fumaric acid yielding acetylene. These are, of course, simple cases ; but even that seemingly unsolvable problem, the constitution of camphoric acid, has been attacked by Walker, and by means of electrolysis of it and its derivatives he has obtained results which must be of great value in ultimately deciding what is the correct formula for this substance.

Iodoform can now be produced in a state of great purity by electrolysing a solution of potassium iodide and sodium carbonate to which alcohol has been added. On electrolysis, employing electrodes of platinum, iodine is continually set free at the anode, and coming in contact with the alcohol at the moment of its liberation produces iodoform. As the reaction proceeds some of the iodine becomes converted into hydriodic acid, and this combines with the alkali liberated at the kathode, or which has been added to the bath, potassium iodide being regenerated, which by the further passage of the current is again split up. The process is a continuous one, the iodoform being from time to time removed and a further quantity of alcohol, potassium iodide and sodium carbonate added. It is interesting to note that the alcohol cannot be replaced by acetone, as in this case only a very small quantity of iodoform is produced. Chloroform and bromoform have not been successfully prepared by this method. Chloral can, however, be produced by electrolysis of a solution of potassium chloride at 100°, to which alcohol is from time to time added.

By the electrolysis of nitrobenzene in a strongly acid alcoholic solution, aniline is produced. If the nitrobenzene is suspended in concentrated hydrochloric acid, ortho- and para-chloraniline are formed. By electrolysis under other conditions, azobenzene, hydrazobenzene or azoxybenzene are obtained.

By the electrolytic oxidation of aniline, dye products can be obtained the nature of which depends upon the solution employed, the strength of the current and the material of the electrode, *e.g.* if an aqueous solution of aniline hydrochloride, which may be either acidified with sulphuric acid or be practically neutral, is electrolysed, platinum electrodes being employed, a green precipitate is produced at the anode, which becomes violet, bluish-violet and finally almost black, practically the theoretical quantity of aniline black having been formed. If the aniline contain toluidine, then mauveaniline, rosaniline, &c., are produced.

Attempts have been made to obtain alizarine by electrolysis of anthraquinone in strong alkaline solution ; indeed, small quantities are said to have been obtained.

It has even been found possible to utilise electricity in the dyeing of cloth. When, *e.g.* a piece of cloth is soaked in a solution of aniline sulphate and placed between two metal plates, which are connected with opposite ends of a dynamo, and the current passed, the aniline sulphate is converted into aniline black ; indeed, by altering the strength of the solution and the density of the current, shades varying from green to deepest black can be produced.

In the case of indigo the cloth is thoroughly impregnated with a thin paste of indigo-blue and caustic alkali ; it is then placed between two metal electrodes. On the current being passed, the insoluble indigo-blue is converted by reduction into the soluble indigo-white, which on exposing the cloth to the action of air becomes again oxidised and the material dyed blue. Patterns may be printed on the cloth by cutting or stamping the plates in relief, or by connecting one pole to a metal plate and the other to a metallic pencil, when patterns, &c., can be readily sketched upon the material (Goppelsroeder).

Such processes as have been described in these articles appear, when seen in print, as extremely simple. Theoretically they may be so ; but in practice, the carrying out of these seemingly simple operations is often attended by great difficulties. For example, the temperature must not be allowed to rise too high or fall too low. The quantity of current and its potential require often to be kept within extremely narrow limits, as the following simple example illustrates.

Silver and copper can be separated by means of electrolysis, the silver alone being deposited if a very low current density (·10 ampere) is employed, whereas with a higher density (·50–1·0 ampere) the copper is deposited. Naturally, then, if at the commencement of the operation the higher current density is employed, both metals will be deposited together. Many of the difficulties to be overcome are to a large extent engineering. And it is to a considerable extent due to collaboration of chemis s and engineers that the science of electro-chemistry has become what it is.

Electro-chemistry is quite in its childhood, but it is making marvellous and rapid progress. Works dealing with technical chemistry but a few years old require to be revised, owing to the alterations which this branch of chemical industry has brought about.

It is humiliating to realise that in this country there is hardly a book on the subject to be obtained, and in most cases even these are only translations from Continental works. And it is to be feared that unless this branch of chemistry becomes more studied than it has been up to the present, we shall find in the near future that electro-chemistry, both theoretical and practical, is the property of America and the Continent.

<div style="text-align:right">F. MOLLWO PERKIN.</div>

ROAD LOCOMOTION.[1]

THE author commenced by saying that the subject of mechanical propulsion upon common roads had now reached a point when it deserves the very careful consideration of mechanical engineers.

For many years the uses and importance of the traction engine have become more and more recognised, but its work covers only a portion of the field for mechanical propulsion on roads, and he went on to consider what has led to a general revival of a movement for lighter road-locomotives which about seventy years ago, in the days of Hancock and Gurney, reached a point that for a time appeared to be leading to permanent results of the most important kind, but which ended in complete failure. In one sense this revival is undoubtedly due to the passing of the Locomotives on Highways Act in 1896, previous to which, for more than twenty years, a law had existed which made it impossible for any self-propelled vehicle to proceed at a rate of more than four miles an hour. The immediate cause of the passing of this Act was the attention aroused in this country by the successful introduction of the motor vehicle for purposes of pleasure in France. The real causes of the present movement were probably to be traced to the gradual feeling amongst all classes of the community that modes of transport, both for purposes of pleasure and business, on the roads had not kept pace, or indeed had made little progress at all, compared with the great changes which had been effected

[1] Abstract of a paper read before the Institution of Mechanical Engineers by Prof. Hele-Shaw, F. R S., April 26.